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THE RELATION OF MATURITY OF THE GRAPES TO THE YIELD, COMPOSITION, AND QUALITY OF RAISINS¹

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THAT THE MATURITY of grapes is related to the yield and quality of the raisins made from them has probably been observed almost as long as grapes have been dried to preserve them. Apparently, however, no one attempted to determine precisely the nature and magnitude of these relationships before the work done by Bioletti (1915),³ which was begun about 1913. Important contributions have since been made by Lyon (1920, 1924), Cruess and Christie (1921), and Nichols and Christie (1930).

Bioletti (1915) reports on tests made with Muscat of Alexandria and Sultanina (Thompson Seedless) at Kearney Park, near Fresno, and at Davis, during the seasons of 1913 and 1914. With Muscat, the drying ratios reported ranged from 4.8 for grapes of 18° Balling to 3.1 for grapes of 28° Balling. Quality, as measured by the size of the individual raisins, improved notably as maturity advanced. With Sultanina, the drying ratios ranged from 4.6 for grapes of 20° Balling to 3.6 for grapes of 24° Balling. According to Bioletti's calculations, the average increase in crop per Balling degree of sugar in the grapes was about 5.35 per cent with Muscat and 7.4 per cent with Sultanina. In another paper Bioletti (1919) briefly reported, collectively, on the results of several years' tests on the drying of eleven varieties of grapes. He interpreted his results as showing an average increase of 35 pounds of dried grapes per ton of fresh for each added degree of sugar. Actually, his figures show the increase to range from 16 to 104 pounds, the greater increases being obtained from the riper fruit. Although he recognized that the higher sugar content measured in the fresh fruit with advancing maturity is chiefly responsible for the increased yield, he was led by his earlier ex-

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³ See "Literature Cited" for complete data on citations, referred to in the text by author and date of publication.

periments to believe that something other than sugar must be a factor in producing the larger increases as maturity became advanced. Lyon's (1920) figures for "Sultana" and "Zante currant" raisins also fluctuate between rather wide limits, but fail to show any consistent trend toward greater increases in yield of raisins per degree Balling as the maturity of the fresh fruit advanced.

In 1926, Bioletti began a more elaborate investigation in collaboration with Christie⁴ and the present author. The work has been continued down to the present time, and this paper will present the principal results.⁵

SOURCES OF THE FRUIT

During the 1926 season, lots of grapes were picked at weekly intervals, August 22 to October 17 inclusive, from about thirty vines in a vineyard near Marysville. For the 1927, 1935, and 1936 series of tests, all fruit was obtained from the University of California vineyards at Davis. Each season, except 1926, two adjacent rows of twenty vines each were chosen as sources of the fruit, one row having been thinned to a light-to-moderate crop, the other being permitted to bear a moderate-to-heavy crop. Pickings were made at approximately weekly intervals, beginning when the fruit was relatively green (for raisins) and extending to the end of the season, when fruit in good physical condition could no longer be obtained. In general, only one large or two medium-sized clusters were harvested from each vine at each picking; and all those from one lot of vines were combined to form a composite sample of 18 kilograms or more.

PREPARATION OF THE SAMPLES FOR DRYING

Except the natural sun-dried lots of 1926 and 1927, all samples were prepared as follows: The individual berries were clipped from the clusters by cutting the pedicels with scissors. All dried, injured, or discolored berries were discarded. The lot was then thoroughly mixed by repeated gentle pouring from one container to another; in this procedure, metal cans of about 3½ cubic feet capacity were found convenient. After the mixing, a small part of the lot was taken out for the observations and measurements on the fresh fruit; and from the remainder, samples of 1,500 or 2,000 grams each were weighed out for the individual drying tests.

For the natural sun-drying tests in 1926 and 1927, entire clusters were used; the individual lots varied in fresh weight from 7 to 15 kilograms.

⁴ A. W. Christie, Assistant Professor of Fruit Products and Associate Chemist in the Experiment Station, University of California; resigned 1928.

⁵ Some of the data obtained in 1926 were published by Nichols and Christie (1930).

Samples for measurements on the fresh fruit were obtained by clipping off a few berries from the basal, middle, and apical portions of each cluster.

MEASUREMENTS ON THE FRESH FRUIT

Weight of One Hundred Berries.—The berry weight was determined by counting out and weighing single lots of 1,000 berries in 1926; single lots of 500 in 1927; and duplicate, triplicate, or quadruplicate lots of 200 each in 1935 and 1936. This last procedure proved to be the most reliable; if the weights of the duplicate lots failed to agree within reasonable limits, additional lots were counted, weighed, and included in the computation. In each case, the results were calculated to weight per 100 berries.

Balling.—Part of the composite sample was thoroughly macerated in a pan by means of a wooden masher or by passing it through a continuous screw-press, and the juice was extracted from the macerated pulp by squeezing or straining through cheesecloth. The juice was poured into glass jars, where it was allowed to stand for a few minutes to permit the escape of air bubbles and settling of the gross sediment. Balling (or Brix) hydrometers, graduated in $\frac{1}{10}$ degrees, were used in glass cylinders of appropriate size. All determinations were made in duplicate or triplicate, and the readings corrected for temperature differences.

Acidity.—The juice extracted for the Balling test was allowed to stand until part of it had become reasonably clear, but never for more than an hour. Duplicate 10-cc portions of the clear juice were then titrated with standardized NaOH solution, phenolphthalein serving as an indicator. A faint color, lasting 10 seconds or longer with constant shaking, was taken as the end point. The results were calculated and expressed as per cent tartaric acid by weight.

METHODS OF DRYING

During the investigation, standard commercial methods of pretreatment and drying were employed; and, in addition, the standard methods were duplicated with either dehydrated or naturally dried lots. The various methods used are briefly described below; the years in which the method was used are indicated.

(1) Natural sun-drying, in 1926, 1927, 1935, and 1936: The grapes were thinly spread, without pretreatment, on trays and exposed to direct solar radiation until dried to the desired degree. In 1926 and 1927, standard wood raisin trays (2×3 feet) were used, and the raisins dried in the open. Since, however, losses were caused by bees and birds, a large cage of $\frac{3}{16}$ -inch mesh hardware cloth was used in 1935 and 1936, and the raisins were dried on paper-covered laboratory-dehydrater trays

inside the cage. The losses were thus practically eliminated. The product was similar to the natural sun-dried raisins of commerce.

(2) Dehydration without pretreatment, in 1926, 1927, 1935, and 1936: The sample was spread on a paper-lined tray, without pretreatment, and dehydrated in a laboratory dehydrator of the recirculating tunnel type, electrically heated and thermostatically controlled to a minimum of 130° F and a maximum of 140°. The rate of air flow exceeded 600 lineal feet per minute between the trays. Humidity, although kept low, was not controlled within close limits. As the desired degree of dryness in the raisins was approached, the trays were weighed at 1- or 2-hour intervals. The end point in drying was determined by assuming a water content of 15 per cent in the dried raisins and by assuming that the Balling reading on the juice of the fresh grapes would indicate the total solids of the grapes. Then the constant 85 (100 minus 15) divided by the Balling of the fresh grapes approximates the drying ratio. The weight of fresh fruit divided by the drying ratio is the calculated weight of the raisins, which was taken as the end point of the drying. The raisins were uniform grayish brown in color, rather tough-textured, and slightly caramelized to the taste.

(3) Lye dip with dehydration, in 1926 and 1935: The grapes were dipped in a 0.2 to 0.3 per cent NaOH solution at a temperature of 95° to 100° C for 2 or 3 seconds—until faint checks showed in the skins after the grapes had been cooled by rinsing in cold water. The sample was then dehydrated as for (2). The raisins were uniform medium brown in color, and otherwise resembled the commercial product occasionally made in this manner.

(4) Lye dip with sun-drying, in 1935: The sample was dipped as for (3) and sun-dried as for (1). The raisins were dark brown, tender, meaty, and slightly sticky—generally similar to the commercial product occasionally made by this process.

(5) Golden bleach, in 1935 and 1936: The hot lye dipping as for (3) was followed by exposure at ordinary air temperature to SO₂ gas (diluted to about 1 per cent by weight with air) until the grapes had bleached to a yellowish white, the fruit absorbing 1,200 to 2,000 p.p.m. of SO₂. They were then dehydrated as in (2). In these experiments the procedure differed in two minor respects from the standard commercial process: first, the SO₂ for bleaching the grapes was derived from the commercial liquefied product instead of from burning sulfur; second, the dehydration temperature was lower, since commercial dehydrators usually operate at about 160° F. The product was of brilliant, glossy, greenish-yellow to golden-yellow color.

(6) Sulfur bleach, in 1935 and 1936: The grapes were treated as for

(5), then exposed to direct sunlight until half or two-thirds dried. The drying was finished in the shade. Exposure to direct sunlight was for a longer period than is usual in commercial practice. Except in being a pronounced reddish-yellow, the raisins were similar to the commercial product.

(7) Australian mixed dip with dehydration, in 1935: The dip was composed of 0.3 per cent NaOH, 0.5 per cent K_2CO_3 , and 0.4 per cent virgin olive oil, this last being first emulsified in a 5 per cent K_2CO_3 solution. It was used at 80° – 82° C, and the grapes were immersed until faint checks showed in the skin after cooling without rinsing—a matter of 2 or 3 seconds. Dehydration was as described for (2). The raisins resembled those of (3) in color, but were more glossy; the texture was more tender than with those of (3). The process is not used commercially.

(8) Australian mixed dip with rack-drying, in 1935 and 1936: The predrying treatment was as for (7). The grapes were dried in the shade on specially constructed wire racks like those commonly used in Australian drying yards. The dip and the drying procedure were essentially the same as described by Lyon (1934). The day after the grapes were placed on the racks, and thereafter at weekly intervals until dry, they were lightly sprayed with a 5 per cent solution of K_2CO_3 in which 0.4 per cent olive oil had been emulsified. The raisins were of soft, tender texture, of characteristic flavor; and the color varied from light to dark brown, the darker colors developing in samples subjected to foggy or rainy weather at some time during the drying period.

(9) Australian cold dip with dehydration, in 1935: The dip was composed of a 5 per cent solution of K_2CO_3 (technical grade) in which was emulsified 0.4 per cent virgin olive oil. It was used at about 35° C, and the grapes were immersed until about three fourths of the bloom had been removed—usually 1 to 4 minutes. The drying was as for (2), and the dried product resembled that of (7). This process is not used commercially.

(10) Australian cold dip with rack-drying, in 1935 and 1936: The predrying treatment was as for (9), and the drying as for (8). The composition of the dip and the drying procedure were essentially the same as that recommended by de Castella (1925). The product varied from light greenish brown to medium brown and in other respects resembled that of (8), but had somewhat better texture. This and (8) are the processes used in making the "Sultana" raisins of Australia and South Africa.

(11) California soda-oil dip with dehydration, in 1935: The dip consisted of a 4 per cent water solution of Wyandotte (soda ash) powder on which was floated a thin film of olive oil. It was used at about 35° C.

The grapes were immersed until about three fourths of the bloom had been removed—usually 30 to 60 seconds. They were dehydrated as for (2). The dried product resembled that of (7). This process is not used commercially.

(12) California soda-oil dip with sun-drying, in 1935: The predrying treatment was as for (11), the drying as for (1). The process was once used extensively in the Sacramento Valley, but now has been largely abandoned. The raisins were medium brown and otherwise resembled the commercial product.

OBSERVATIONS AND DETERMINATIONS ON THE RAISINS^a

Immediately after the final weighing of the dried raisins, part or all of each lot was packed into a glass preserving jar, sealed, stored for a few days at room temperature, and then held at 1° C until used.

The physical measurements attempted were based largely on the report of Chace and Church (1927) except that moisture was determined by direct vacuum-oven drying. The chemical determinations followed standard practices wherever possible, the methods of the Association of Official Agricultural Chemists (1935) being used as guides.

Drying Ratio.—After the moisture determinations, the dry weight of each lot was adjusted by calculation to a 15 per cent moisture basis. The drying ratio was then calculated by dividing the original fresh weight by the dry weight adjusted to a basis of 15 per cent moisture. Usually, in the tables and discussion following, the quotient only is expressed. The ratio is, however, always implied.

Weight of Raisin Berries.—The sample was loosened up to separate the individual raisin berries from each other, then mixed by slowly rotating the partially filled jar in an end-over-end manner. Duplicate lots of 200 berries each were counted out and weighed. If the weights of the two lots differed by more than 5 per cent, additional lots were taken. The weight of 100 raisin berries was calculated from the total number counted and from their total weight.

Weight per Unit Volume.—The laboratory method of Chace and Church (1927) for this measurement was modified by the use of a home-made mechanical shaker. A calibrated 500-cc wide-mouth Erlenmeyer flask was filled to overflowing with loose raisins. The flask was then placed in a receptacle on the shaker, which was so constructed as to provide an abrupt vertical drop of about $\frac{1}{4}$ inch at the rate of 120 times per minute. The shaker was run for $1\frac{1}{2}$ minutes with each sample. The flask was large enough so that when the shaking was finished most of the

^a Most of the routine work of chemical analysis on the 1935 and 1936 raisin samples was done by Bernard A. Fries.

samples slightly overran the 500-cc volume mark. The volume was adjusted to the mark by removing or adding a few raisins as necessary. All determinations were made in duplicate; and the duplicates checked, in all but occasional instances, within 2 per cent of each other. Where greater differences occurred, the determinations were repeated. Satisfactory checks could not be obtained by hand-shaking nor on the mechanical shaker with less than $1\frac{1}{2}$ minutes' shaking. The weights obtained for 500 cc are heavier than those reported by Chace and Church.

Mold and Fermentation.—The hydrogen peroxide test described by Chace and Church (1927) for mold and fermentation was used on a sample of 100 raisin berries from each lot. Since the amount of mold and decay observed appeared to be correlated only with weather conditions during drying and with the method of drying, not with the maturity of the grapes, the data are not reported; but lots in which more than 10 per cent of the berries showed evidence of mold or yeast growth were discarded.

Moisture in the Raisins.—A portion of 250 grams or more of the original raisin sample was passed four times through a small household-type food chopper with a nut-butter attachment. The ground sample was then sealed in a glass sample jar, and from it portions were withdrawn for all determinations requiring ground material.

The moisture test was made as follows: Filter papers of 9-cm size were oven-dried at 80° C for 8 hours, cooled in a desiccator over soda lime, and weighed in a tared, closed petri dish. About 5 grams of the ground raisin pulp was quickly and thinly spread by means of a spatula on the paper, which was rested on a glass plate; then the paper, now holding the sample, was again weighed in the petri dish. The operations of placing the sample on the paper and replacing the paper in the petri dish were performed as quickly as possible in order to minimize changes in weight due to moisture absorption or loss. The drying was done in a vacuum oven at 70° C for 12 hours, under a pressure approximating 100 mm mercury, with a slow current of dried air passing through the oven. The dried samples, cooled in a desiccator over soda lime, were finally weighed in the closed petri dish. Determinations were in duplicate. In comparisons made during the preliminary work, the method yielded more consistent results with much less labor than the Association of Official Agricultural Chemists' official method (1935) making use of asbestos. The end point was essentially the same as that obtained by using the official procedure and drying for 10 hours. Consistent results could not be obtained by the official method with only 6 hours' drying.

Sugar Content of the Raisins.—Determinations of sugars on the 1926 samples (by the Fruit Products Laboratory at Berkeley) were made as

follows: A 10-gram portion of the ground sample was extracted by boiling in 500 cc water, filtered, then cleared with Horne's basic lead acetate and sodium oxalate. Copper oxide precipitated by the regular Munson and Walker procedure was determined by the Shaeffer-Hartman (1920) method. With the 1927 samples, 5 grams of raisins were extracted with 95 per cent alcohol in Soxhlet apparatus. The extract, brought to sirupy consistency under reduced pressure, was taken up in water, and the determination made thenceforth as with the 1926 samples. The results were less consistent than was desired.

With the 1935 and 1936 samples, the determination of total water-insoluble matter was included, and the following procedure of extraction gave satisfactory results: Filter papers, 15 cm in diameter, were dried and weighed as for the moisture determinations. Before drying, the paper was folded to make a roughly conical receptacle that could be inserted in a Soxhlet extraction tube with the top edge above the high point in the siphon. About 10 grams of the ground raisin pulp was smeared on the inside of the paper cone and weighed, then placed in the extraction tube so that the drip from the condenser fell directly into the paper cone containing the sample. Extraction was with water for 6 to 8 hours, the water in the boiling flask being changed two or three times early in the extraction period to avoid "bumping" and partial caramelization of the sugars on the sides of the flask. The several extract portions were combined and made up to 1-liter volume.

An aliquot portion of the extract to be used for the sugar determination was cleared in the usual manner with lead acetate and sodium oxalate. Copper oxide precipitated by the Quisumbing and Thomas method (Association of Official Agricultural Chemists, 1935) was determined by direct weighing. Very close agreement was obtained from determinations on duplicated samples.

Since preliminary tests showed no sucrose to be present, only reducing sugars were determined.

Water-Insoluble Solids in the Raisins.—The residue in the filter paper, after the extraction described above for the 1935 and 1936 samples, was dried at 80° C for 8 hours, cooled in a desiccator, and weighed in a closed petri dish.

Titrateable Acid in the Raisins.—The total titrateable acidity was determined by titrating 100-cc portions of the extract (made up to 1-liter volume) with 0.033 *N* sodium hydroxide, phenolphthalein serving as the indicator. If the end point was obscured by the brown color of the extract, a spot plate was used.

Potassium, Calcium, Magnesium, and Phosphorus Content.—A 10-gram sample of the ground raisins was charred in a porcelain crucible

over the free flame of a Bunsen burner. About 1 cc of dilute H_2SO_4 was added to the charred mass, which was then ashed at 580°C . Silica was removed by twice evaporating with 1 to 5 HCl . The ash was then dissolved in additional 1 to 5 HCl and made up to 100 cc. Potassium was determined gravimetrically by the platinic chloride method. Calcium was determined, by the official method of the Association of Official Agricultural Chemists (1935), involving precipitation with $\text{NH}_4\text{C}_2\text{O}_4$, redissolving with H_2SO_4 , and finally titration with KMnO_4 . For magnesium determination the filtrate from the calcium precipitation was evaporated to 10-cc volume. Next, 7 cc of microcosmic salt solution was added, and then 10 cc concentrated NH_4OH . After standing overnight the precipitate was filtered off and washed with dilute NH_4OH and alcohol. The precipitate and the paper were then added to 20 cc of 0.02 N H_2SO_4 and digested cold for 3 or 4 hours. The excess acid was titrated with 0.02 N NaOH . Phosphorus was determined colorimetrically by the Fiske and Subbarow method as given by Yoe (1928).

RESULTS WITH THOMPSON SEEDLESS

In most of the following tables and discussions, the individual experimental lots are grouped into classes according to the Balling degree of the juice of the fresh grapes. Thus all Thompson Seedless lots testing between 17.5° and 18.4° were grouped into the class designated 18 in the left-hand column of each table. Class 19 includes all lots from 18.5° to 19.4° ; class 20 those from 19.5° to 20.4° ; and so on to class 29, which includes all lots from 28.5° to 29.7° . The number of lots in each class is shown in the second and third columns of table 1. Dashes in the tables indicate absence of data. All observations and calculations involving the "dry weight" of the raisins are reported on the basis of 15 per cent moisture in the raisins. To aid in analyzing and interpreting the data, standard errors, derived by the formula $\sqrt{\frac{\Sigma d^2}{n(n-1)}}$, are given wherever they appear to have value.

The Relation of the Drying Ratio to the Balling Degree of the Fresh Grapes.—The dry weight of the raisins obtained from a unit quantity of fresh Thompson Seedless grapes increased regularly with advancement in maturity of the grapes. The drying ratios, therefore, vary inversely with the Balling degree of the fresh grapes as shown in table 1. All artificially dehydrated lots, pretreated in various ways as described under "Methods of Drying," have been grouped in the columns of table 1 headed "Dehydrated." Likewise all lots dried without the use of artificial heat, whether dried in direct sunlight or in shade, have been grouped in the "Sun-dried" columns.

The drying ratios of the dehydrated lots were consistently more favorable than those of similar sun-dried lots except in the 28° Balling class, where the difference is negligible but in the opposite direction. The differences between dehydrated and sun-dried lots appear to be slightly greater in the low Balling range than in the high range—that is, 25° Balling and above. The coefficient of correlation of drying ratio with Balling degree of the fresh grapes is -0.962 for the dehydrated and -0.951 for the sun-dried lots (table 5).

TABLE 1
RELATION OF THE DRYING RATIO TO THE BALLING DEGREE OF THE FRESH
GRAPES IN THOMPSON SEEDLESS

Degree Balling of fruit	Number of lots		Drying ratio*		Balling \times drying ratio†	
	Dehy- drated	Sun- dried	Dehydrated	Sun-dried	Dehydrated	Sun-dried
18.....	14	12	4.79 \pm 0.034	4.88 \pm 0.052	85.5 \pm 0.344	87.3 \pm 0.835
19.....	4	2	4.35	4.45	83.9	85.2
20.....	11	6	4.35 \pm 0.036	4.50 \pm 0.053	85.7 \pm 0.584	88.3 \pm 1.016
21.....	13	13	4.04 \pm 0.018	4.17 \pm 0.028	84.9 \pm 0.342	87.4 \pm 0.595
22.....	26	31	3.80 \pm 0.010	3.88 \pm 0.016	83.7 \pm 0.176	85.4 \pm 0.310
23.....	23	27	3.63 \pm 0.012	3.71 \pm 0.027	83.9 \pm 0.160	85.8 \pm 0.297
24.....	17	18	3.47 \pm 0.016	3.57 \pm 0.027	83.7 \pm 0.353	83.3 \pm 0.841
25.....	35	35	3.41 \pm 0.003	3.46 \pm 0.012	84.3 \pm 0.216	85.6 \pm 0.255
26.....	5	0	3.18	—‡	83.7	—
27.....	16	17	3.12 \pm 0.005	3.13 \pm 0.018	83.9 \pm 0.446	83.9 \pm 0.485
28.....	7	8	3.04 \pm 0.021	3.03 \pm 0.015	84.5 \pm 0.276	85.1 \pm 0.377
29.....	3	5	2.79 \pm 0.006	2.82 \pm 0.015	82.9 \pm 0.562	83.8 \pm 0.449
Mean.....					84.21	85.55

* Raisins, 15 per cent moisture.

† Arithmetical means of calculations on individual lots.

‡ Dashes indicate data not available.

In the last two columns of table 1 appear the products of the Balling degree multiplied by the respective drying ratios. The figures given are the arithmetical means of calculations on the individual lots in each class. The mean of these products for all dehydrated lots is 84.21; for all sun-dried lots, 85.55. The figures exhibit no appreciable correlation with maturity. They fall so closely around the mean as to indicate that the relation of the drying ratio to the Balling degree (maturity) of the fresh grapes approximates that of a straight-line function, the value of the constant differing, of course, with the method of drying employed.

The fluctuations were greater in the data on the sun-dried lots than in those on the dehydrated lots, probably because of the lesser degree of control that could be exercised over drying conditions and over sources of minor losses. Direct losses of entire berries were not, however, entirely responsible for the differences shown between the dehydrated and sun-

dried lots, for the raisin berries were slightly heavier in most dehydrated lots than in equivalent sun-dried lots (table 2).

The Relation of the Weight of Berry and the Weight per Unit Volume of the Raisins to the Balling Degree of the Fresh Grapes.—Table 2 gives the weight per 100 raisin berries and the weight per 500-cc volume measurements on the experimental lots, grouped into Balling-degree classes. The figures show, with some irregularities, a gradual and steady increase in the weight of raisin berries and in weight per unit volume as the total soluble-solids content of the fresh grape berries increases. The

TABLE 2

RELATION OF THE BALLING DEGREE OF FRESH GRAPES TO THE WEIGHT OF BERRY AND THE WEIGHT PER UNIT VOLUME OF THE RAISINS, IN THOMPSON SEEDLESS

Degree Balling of fruit	Weight per 100 raisin berries, grams*		Weight per 500 cc volume of raisins, grams	
	Dehydrated	Sun-dried	Dehydrated	Sun-dried
18.....	26.1±0.522	26.0±0.507	316±4.15	310±5.28
19.....	—†	—	—	—
20.....	31.8±0.325	31.0±0.294	324±8.15	329±8.23
21.....	35.8±0.946	35.4±1.153	345±5.03	341±3.71
22.....	38.6±0.771	37.7±0.756	346±4.85	346±3.37
23.....	40.5±0.747	38.9±0.540	344±4.80	356±4.33
24.....	39.6±0.740	38.3±0.866	353±5.63	354±3.19
25.....	43.6±0.638	42.2±0.682	351±4.11	361±3.08
26.....	—	—	—	—
27.....	47.7±1.220	46.7±1.033	360±5.68	365±5.23
28.....	48.1±1.277	44.3±1.179	351±4.43	377±7.09
29.....	44.3±0.537	45.3±1.005	367±6.75	378±7.15

* Data adjusted to the basis of 15 per cent moisture in the raisins.

† Dashes indicate data not available.

increase in weight of raisin berry from 18° to 29° Balling in the fresh fruit was roughly 70 per cent; the increase in weight per unit volume over the same range of maturity, about 18 per cent. The figures of table 2 show small differences in raisin-berry weights between the dehydrated and sun-dried lots in favor of the dehydrated lots by odds of about 150 to 1 when the data are analyzed by Student's (1908, 1917) method. Most of the sun-dried lots appear to have had a higher weight per unit volume than did similar dehydrated lots. Since, however, the figures for dehydrated lots in table 2 lack consistency in respect to this measurement, the odds by Student's method are only 26 to 1 in favor of the sun-dried.

The rather positive, although small, differences in berry weights in favor of the dehydrated lots indicate that respiration, and perhaps fermentation in some lots, used up some of the grape solids in the sun-dried fruit. The data on the sugar content of the raisins (table 3) tend to

substantiate this hypothesis, showing a higher percentage of sugar in the dehydrated than in the sun-dried lots.

The coefficient of correlation of raisin-berry weight with Balling degree of the fresh fruit was 0.860 for the dehydrated lots, and 0.699 for the sun-dried. The coefficient of correlation of the weight per unit volume measurements on the raisins with the Balling degree of the fresh fruit was 0.454 for the dehydrated, 0.625 for the sun-dried lots (table 5).

The Relation of the Composition of the Raisins to the Balling Degree of the Fresh Grapes.—The sugar content of the raisins increased with

TABLE 3
RELATION OF BALLING DEGREE OF THE FRESH GRAPES TO THE SUGARS AND
INSOLUBLE SOLIDS OF THE RAISINS, IN THOMPSON SEEDLESS*

Degree Balling of fruit	Per cent sugars†		Per cent insoluble solids‡	
	Dehydrated	Sun-dried	Dehydrated	Sun-dried
18.....	69.5±0.246	68.7±0.313	6.38±0.166	7.06±0.233
19.....	—§	—	—	—
20.....	70.4±0.829	69.6±0.584	7.05±0.403	6.66±0.178
21.....	70.9±0.295	71.0±0.246	6.23±0.254	6.12±0.132
22.....	72.0±0.218	71.2±0.360	5.60±0.141	5.91±0.064
23.....	72.3±0.173	71.4±0.282	5.70±0.135	5.65±0.062
24.....	72.8±0.347	71.5±0.520	5.83±0.259	5.69±0.074
25.....	72.7±0.169	71.9±0.363	5.26±0.107	5.29±0.070
26.....	—	—	—	—
27.....	72.9±0.233	71.5±0.273	4.87±0.086	5.29±0.083
28.....	72.2±0.541	71.0±0.313	5.15±0.322	5.08±0.129
29.....	73.0±0.276	71.7±0.458	4.52±0.076	4.98±0.172

* Data adjusted to the basis of 15 per cent moisture in the raisins.

† Reducing sugars calculated as invert sugars.

‡ Insoluble residue from water extraction in the Soxhlet apparatus.

§ Dashes indicate data not available.

the maturity of the grapes during the early part of the maturation period—from 18° to 23° or 24° Balling (table 3). After the grapes had reached 24° Balling, the sugar content of the raisins apparently increased but little, if at all. At 18° Balling the sugar content of the raisins was 69.5 per cent and 68.7 per cent, respectively, for dehydrated and sun-dried lots; whereas at 24° Balling it was 72.8 per cent and 71.5 per cent, respectively, calculated as invert sugars and based on raisins of 15 per cent moisture content.

The dehydrated lots had higher sugar content than the sun-dried by 1.3 per cent of the sun-dried.

The coefficient of correlation of sugar content of the raisins with the Balling degree of the fresh grapes over the entire range of maturity studied was 0.474 in the dehydrated, 0.394 in the sun-dried lots (table 5).

The water-insoluble solids of the raisins varied inversely with the sugars, decreasing, as maturity advanced, from about 7.0 per cent in

the raisins made from grapes of 18° or 19° Balling to about 5.7 per cent at 23° or 24° Balling and to about 5.0 per cent in the raisins made from the ripest grapes. The differences in insoluble-solids content shown in table 3 between the dehydrated and sun-dried lots are not significant.

The coefficient of correlation of insoluble solids in the raisins with the Balling degree of the fresh fruit was -0.460 in the dehydrated lots, -0.693 in the sun-dried (table 5).

The total titratable acidity of the raisins decreased markedly with increased maturity of the fresh grapes in the early part of the ripening

TABLE 4

RELATION OF BALLING DEGREE AND TITRATABLE ACID IN THE FRESH GRAPES TO THE TITRATABLE ACID IN THE RAISINS, IN THOMPSON SEEDLESS

Degree Balling of fruit	Per cent acid in fresh fruit*	Percentage of acid in fresh fruit \times drying ratio†		Per cent acid in raisins*‡	
		Dehydrated	Sun-dried	Dehydrated	Sun-dried
18.....	0.79	3.82±0.027	3.92±0.041	3.47±0.111	3.37±0.123
19.....	—§	—	—	—	—
20.....	0.69	3.06±0.025	3.13±0.037	2.81±0.133	2.88±0.261
21.....	0.66	2.69±0.012	2.76±0.018	2.45±0.077	2.47±0.084
22.....	0.59	2.16±0.006	2.26±0.009	2.16±0.070	2.11±0.052
23.....	0.54	1.85±0.007	1.94±0.015	1.91±0.083	1.93±0.050
24.....	0.51	1.71±0.008	1.88±0.014	1.83±0.098	1.92±0.095
25.....	0.46	1.52±0.002	1.61±0.006	1.70±0.043	1.70±0.040
26.....	—	—	—	—	—
27.....	0.42	1.26±0.002	1.37±0.008	1.59±0.061	1.55±0.050
28.....	0.42	1.24±0.009	1.30±0.006	1.68±0.098	1.49±0.092
29.....	0.44	1.24±0.003	1.26±0.007	1.62±0.163	1.47±0.056

* Per cent acid by weight calculated as tartaric acid.

† Means of computations on individual lots.

‡ Water extract titrated with 0.033 normal NaOH to phenolphthalein indicator and calculated as tartaric acid.

§ Dashes indicate data not available.

period (table 4). As the grapes became more mature, the decrease in acidity of the raisins became less. Titration figures on the fresh grape juice (table 4, second column) show a similar trend. The total acid content of the fresh grapes appears to decrease rapidly early in the ripening period, but more slowly or not at all later on.

To judge from the rather rapid decrease in the total titratable acid content of the raisins in the early part of the ripening period of the grapes, a method of grading raisins for quality on the basis of acid determination on the raisin pulp may have considerable practical value.⁷ It apparently provides an index of the approximate maturity of the grapes within the range of its application, which is indicated in this investigation to be between 18° and 23° Balling.

⁷ Such a method has been proposed by Mr. Charles D. Fisher of the Dried Fruit Association of California (unpublished).

The coefficient of correlation of the total titratable acidity of the raisins with the Balling degree of the fresh grapes was -0.741 for the dehydrated, -0.777 for the sun-dried lots (table 5).

Table 4 shows no consistent differences in acid content between the dehydrated and sun-dried raisins. (The odds are only 8.9 to 1, by Student's method, that the dehydrated lots as a group are higher.)

Table 4 gives also the titratable acidity of the fresh grapes multiplied by the drying ratio (from table 1) in order that these calculated quantities may be compared with the total titratable acid content as determined on the raisins. As the figures show, in the early part of the ripening period—until the fresh grapes reach 22° or 23° Balling—the

TABLE 5
COEFFICIENTS OF CORRELATION BETWEEN BALLING DEGREE OF THE
FRESH GRAPES AND VARIOUS DETERMINATIONS ON THE
RAISINS, IN THOMPSON SEEDLESS

Determinations	Dehydrated lots	Sun-dried lots
Drying ratio.....	-0.962	-0.951
Sugars.....	0.474	0.394
Titratable acids.....	-0.741	-0.777
Insoluble solids.....	-0.460	-0.693
Weight per 100 raisin berries.....	0.860	0.699
Weight per unit volume.....	0.454	0.625

titratable acid in the raisins is less than the calculated amount, assuming that there was no change in the nature of the acids of the fresh grapes as a result of drying. In the later part of the ripening range—above 22° or 23° Balling—the total acid content of the raisins is consistently greater than the calculated amount. The data are very consistent in both the dehydrated and sun-dried lots, and the reversal of trend in the figures is probably not due to any errors in the empirical procedures followed in titrating either the fresh grape juice or the water extracts of the raisins. The phenomenon may be explained, conceivably, by changes in the composition of the grapes, perhaps precipitation of potassium bitartrate in the grape tissues, part of the precipitate being lost in the discarded fresh grape pulp but redissolved in the prolonged water extraction of the raisin pulp. It has not, however, been possible to make the necessary investigations to verify or disprove this hypothesis.

The content (percentage) of potassium, calcium, and magnesium of the Thompson Seedless raisins appears to remain nearly constant over the entire range of maturity of the grapes used in the investigations (table 6). The data of table 6 appear to indicate that phosphorus may

decrease slightly in the raisins as the maturity of the grapes advances; but the consistency in the figures is not sufficient to establish the apparent decrease as a fact.

The potassium content of the raisins averaged 0.905 per cent, the calcium 0.058 per cent, the magnesium 0.027 per cent, and the phosphorus 0.105 per cent.

TABLE 6

RELATION OF BALLING DEGREE OF THE FRESH GRAPES TO THE POTASSIUM, CALCIUM, MAGNESIUM, AND PHOSPHORUS CONTENT OF THE RAISINS, IN THOMPSON SEEDLESS*

Degree Balling of fruit	Potassium (per cent K)		Calcium (per cent Ca)		Magnesium (per cent Mg)		Phosphorus (per cent P)	
	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried
18.....	0.862	0.891	0.061	—†	0.026	—	0.115	0.114
19.....	—	—	—	—	—	—	—	—
20.....	0.946	0.935	0.057	0.072	0.029	0.029	0.107	0.108
21.....	0.865	0.864	0.056	—	0.022	—	0.105	0.104
22.....	0.914	0.938	0.052	0.050	0.021	0.029	0.110	0.111
23.....	0.852	0.909	0.059	—	0.020	—	0.107	0.104
24.....	0.935	0.973	0.057	0.051	0.032	0.033	0.107	0.106
25.....	0.871	0.909	0.063	0.066	0.018	0.021	0.106	0.103
26.....	—	—	—	—	—	—	—	—
27.....	0.880	0.898	0.060	0.051	0.030	0.035	0.104	0.106
28.....	0.935	0.966	0.057	—	0.033	—	0.100	0.095
29.....	0.891	0.874	0.050	—	0.020	—	0.097	0.097

* Data adjusted to the basis of 15 per cent moisture in the raisins.

† Dashes indicate data not available.

The Relation of the Balling Degree of the Grapes to Quality in the Raisins.—The weight of the raisin berries and the weight per unit volume⁸ are accepted factors in the measurement of quality in raisins.

The data on weight of berry, weight per unit volume, sugar content, acidity, and insoluble-solids content indicate a continued improvement in the quality of the raisins as the grapes mature, the improvement proceeding rapidly during the early part of the ripening period, slowing in its middle part, and almost ceasing as the grapes become very ripe.

Representative samples from the experimental lots of "naturals" and golden-bleached raisins were submitted to a group representing the principal commercial raisin packers of the state. Tabulation of their grading of the samples showed continuous improvement in quality over the entire ripening range.

⁸ The weight per unit volume measurement, based on the work of Chace and Church (1927), has been used by a large cooperative organization for many years to grade growers' lots of raisins when received at the warehouse. Differential payments have been made upon the basis of this measurement.

The Influence of the Method of Drying on the Drying Ratio, Sugar Content, and Acid Content of Thompson Seedless Raisins.—In tables 1 to 4, inclusive, all dehydrated lots and all sun- or shade-dried lots were grouped together to show the relations existing between the maturity of the fresh grapes and the several factors measured in the raisins. The predrying treatments—dipping and sulfuring—as well as the manner of drying did, however, materially influence the yield and composition of the raisins.

TABLE 7

THE INFLUENCE OF METHOD OF DRYING ON DRYING RATIO, SUGAR CONTENT OF THE RAISINS, AND TOTAL TITRATABLE ACIDITY OF THE RAISINS, IN THOMPSON SEEDLESS

Method of drying	Balling degree \times drying ratio*	Percentage sugar (as invert) in raisins from grapes of 23° Balling	Percentage acid (as tartaric) in raisins from grapes of 23° Balling
(1) Natural sun-drying.....	87.8	70.4	1.88
(2) Dehydration without pretreatment.....	84.5	72.2	2.01
(3) Lye dip with dehydration.....	84.1	72.2	1.86
(4) Lye dip with sun-drying.....	85.5	71.9	1.77
(5) Golden bleach.....	83.6	72.5	2.41
(6) Sulfur bleach.....	85.0	72.3	2.34
(7) Australian mixed dip with dehydration.....	84.3	72.2	1.83
(8) Australian mixed dip with rack-drying.....	85.0	71.7	1.80
(9) Australian cold dip with dehydration.....	84.1	72.3	1.61
(10) Australian cold dip with rack-drying.....	85.0	70.7	1.77
(11) California soda-oil dip with dehydration.....	84.5	72.3	1.56
(12) California soda-oil dip with sun-drying.....	86.4	71.3	1.86

* Means of the products calculated individually for each lot by multiplying the Balling degree by the drying ratio. Dividing the quantities given in this column by any Balling degree, from 18° to 29°, gives the approximate drying ratio obtained with Thompson Seedless grapes at that degree Balling for the respective method of drying.

Table 7 shows how the several treatments used and the manner of drying affected the product of the Balling degree multiplied by the drying ratio, the sugar content of the raisins, and their total titratable acidity. The Balling degree \times drying ratio figures are averages of the quantities obtained by calculating this product separately for each lot dried by the respective methods. It is a convenient expression since the drying ratio obtained with Thompson Seedless grapes at any given Balling degree between 18° and 29° can be very closely approximated by simply dividing it by the Balling degree. The percentages of sugar and acid are given in table 7 only for raisins made from grapes of 23° Balling. The differences obtained in sugar and acid among the various methods of drying, increased slightly with grapes of lower degree Balling but remained fairly constant above 23° Balling. Means calculated from the figures given in table 7 for methods of drying involving arti-

ficial dehydration and for methods involving sun- or shade-drying will be found to differ slightly from the figures given in tables 1, 3, and 4. The apparent inconsistencies do not indicate discrepancies in the data nor in their interpretation but are the result of not having the same number of lots represented in each method of drying. Methods 4, 7, 9, 11, and 12 were used only during the 1935 season, hence fewer lots dried by these methods than by the other methods are represented in tables 1, 3, and 4.

The dehydrated lots all yielded better drying ratios, as indicated by lower values for Balling degree \times drying ratio, than equivalent sun- or rack-dried lots. All methods involving a predrying treatment gave better ratios than natural sun-drying. The most favorable ratios were obtained with the golden bleach (method 5), but the advantage of this method over others involving dehydration is small. Hot lye dipping improved the drying ratio in the sun-dried lots, and the sulfured lots (methods 5 and 6) came out slightly more favorably than those lye dipped but not sulfured (methods 3 and 4). The potassium carbonate and oil dips (methods 7 to 10) were roughly equal to the hot lye dip in their effect on drying ratio. Differences of less than 0.5 in the Balling degree \times drying ratio are not significant.

The golden-bleached raisins (method 5) had the highest apparent sugar content. In the percentage-sugar column of table 7, differences of less than 0.5 are not significant. No differences may be assumed to exist, therefore, among equivalent lots dried according to methods 2, 3, 4, 6, 7, 9, and 11; all of these are, however, definitely higher than the natural sun-dried, but the differences between any of these methods and method 5 are of doubtful significance. The raisins made by methods 8 and 12 (table 7) are intermediate in sugar content, higher than the natural sun-dried, and lower than the golden bleached. Method 10 produced raisins of about the same sugar content as the "naturals" (method 1).

The sulfured lots (methods 5 and 6) are clearly higher in titratable acid than any others. No determinations for SO_2 were made; but, assuming the raisins to be analogous to similar commercial samples, a reasonable estimate of the SO_2 in them would approximate 1,000 parts per million (0.1 per cent). If the SO_2 present was all titratable, which it probably is not, and was expressed in terms of tartaric acid, it would account for about 0.23 per cent acid or slightly less than half of the difference found between the golden-bleached raisins (method 5) and those of method 3, which had no sulfur dioxide but which were otherwise treated similarly. The remainder of the apparent differences shown between methods 5 and 3 and methods 6 and 4 are unaccounted for. Differences of 0.12 or greater in the total-acid column of table 7 are required for significance (20 to 1 odds). The strong carbonate dips of

methods 9 and 11 reduced the apparent acid content of the raisins, probably as a result of surface adherence of some of the dipping solution. These raisins were not washed after drying. The raisins of methods 10

TABLE 8

THE RELATION BETWEEN THE SIZE OF CROP, MATURITY, AND SIZE OF BERRY IN
THOMPSON SEEDLESS GRAPES, AT DAVIS

Picking date	Degree Balling	Weight per 100 berries, grams	Degree Balling	Weight per 100 berries, grams
1927	Vines of moderate crop (6 tons per acre)		Vines of heavy crop (9 tons per acre)	
September 6.....	22.5	128	20.3	119
September 10.....	23.0	131	21.4	120
September 17.....	23.0	130	22.3	118
September 24.....	24.3	135	22.2	121
October 1.....	25.0	133	23.4	120
October 8.....	26.1	139	23.7	122
October 15.....	27.0	137	24.5	122
October 22.....	26.5	140	—*	120
1935	Vines of moderate crop (7 tons per acre)		Vines of heavy crop (12 tons per acre)	
August 31.....	21.0	129	18.2	127
September 7.....	19.6	130	17.4	120
September 13.....	22.1	136	21.0	136
September 20.....	23.8	142	21.9	161
September 27.....	23.4	138	22.4	152
October 4.....	24.6	144	23.0	169
October 11.....	24.4	143	24.8	157
October 18.....	24.3	144	24.6	167
1936	Vines of light crop† (3 tons per acre)		Vines of moderate crop (6 tons per acre)	
August 22.....	21.9	130	21.6	134
August 29.....	24.4	140	22.9	137
September 4.....	24.5	144	23.3	137
September 11†.....	26.8	136	24.8	136
September 18.....	28.0	136	25.1	134
September 25.....	29.7	137	26.5	138
October 2.....	—	—	27.0	139

* Dashes indicate data not available.

† The first three pickings exhausted the supply of fruit on the vines used August 22 to September 4, inclusive. Another group of vines was used to supply the fruit for the September 11 to September 25 tests from the light-crop vines.

and 12, which received predrying treatments identical with those of methods 9 and 11 respectively, were washed after drying. They show no considerable decrease in acidity resulting from the treatment. The differences in acid content between dehydrated and equivalent sun-dried lots is small except in the lots dried by method 9 as compared with 10 and

those of method 11 as compared with 12. The probable reason for these differences has already been explained.

The Relation Between Size of Crop, Maturity, and Size of Berry.—Table 8 shows the picking dates and Balling degree of the fresh grapes, and the weight per 100 berries for each series of experimental lots obtained from the vineyards at Davis. The crop weights given in the table were arrived at by adding together all quantities removed from the vines, plus the estimated amount of fruit remaining unharvested at the end of the season, and then calculating to the acre basis.

The data are inconclusive. The figures show that in 1927 the vines carrying the heavy crop were a little slower in ripening their fruit and produced somewhat smaller berries than did the vines having only a moderate crop. Also, the berries from the moderately loaded vines apparently increased in size, at least during the early part of the ripening period, whereas those from the heavily loaded vines did not.

In 1935, the fruit from the heavily loaded vines was a little greener early in the season, but caught up with that from the moderately loaded vines before the season was over. The berries from both lots of vines increased in size during the early part of the ripening season, and after the third picking those from the heavily loaded vines were larger than those from the moderately loaded vines.

In 1936, two different sets of lightly loaded vines were required to supply the needed quantity of fruit. The two groups of vines were very similar, but not identical in their characteristics, as is indicated by the break in berry-size increase when the change to the second set of vines was made on September 11. The fruit on the lightly loaded vines ripened slightly ahead of that from the moderately loaded vines. Some increase in berry size is indicated as ripening progressed in the fruit from the first set of lightly loaded vines, but none is indicated in the second set of lightly loaded vines nor in the moderately loaded vines.

RESULTS WITH MUSCAT OF ALEXANDRIA

The work with the Muscat paralleled that with Thompson Seedless during the 1935 and 1936 seasons, but involved a total of only 76 individual lots as against a total of 348 (in four years) for Thompson Seedless. The data obtained are therefore less extensive and not so consistent when summarized. The methods of drying used were those described for Thompson Seedless as (1) natural sun-drying; (2) dehydration without pretreatment; (3) lye dip with dehydration; (4) lye dip with sun-drying; (9) Australian cold dip with dehydration; and (10) Australian cold dip with rack-drying. The complete series was carried through 1935; but in 1936 it was impossible to follow the entire program, and

TABLE 9
RELATION OF BALLING DEGREE TO CERTAIN DETERMINATIONS ON THE FRESH GRAPES AND RAISINS, IN MUSCAT OF ALEXANDRIA *

Degree Balling of fruit	Fresh fruit		Raisins										
	Per cent acid, as tartaric	Weight per 100 berries, grams	Number of lots		Drying ratio		Drying ratio × Balling degrees		Weight per 100 raisin berries, grams		Weight per 500 cc raisins, grams		
		1935	1936	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried
16.0.....	0.69	423	—†	3	2	4.95	4.92	79.0	78.7	84	83	284	297
17.1.....	0.66	407	—	3	2	4.68	4.70	79.9	80.4	90	86	310	305
18.6 and 18.7.....	0.59	400	382	5	4	4.23	4.45	79.9	83.0	91	90	323	297
19.1 and 19.2.....	0.45	435	—	6	3	4.16	4.30	78.9	82.5	109	107	298	306
19.7 and 20.6.....	0.43	491	390	5	3	3.89	4.08	78.7	81.6	112	104	306	304
21.3 and 21.4.....	0.44	480	405	5	3	3.78	3.86	80.7	82.4	120	111	309	309
22.4 and 22.7.....	0.36	454	—	5	1	3.61	3.83	81.6	86.9	132	120	317	322
23.1 and 23.3.....	0.38	403	—	4	2	3.51	3.60	81.3	83.8	116	113	315	321
24.7 and 25.4.....	0.39	—	405	8	2	3.27	3.37	82.0	84.5	123	119	316	330
27.0 and 27.5.....	0.37	—	393	6	4	3.00	3.06	81.9	84.1	130	129	323	331

* Data adjusted to the basis of 15 per cent moisture in the raisins.

† Dashes indicate data not available.

methods 9 and 10 were dropped. A considerable number of the sun-dried lots were discarded in which 10 per cent or more of the berries showed a positive reaction to the yeast and mold test with hydrogen peroxide.

Tables 9 and 10 summarize the results. The individual lots are grouped according to the Balling degree of the fresh fruit; but, since each class represents only one or two series, the actual Balling hydrometer readings are given in the left-hand column of each table. The acid titrations, calculated to per cent by weight as tartaric, are averaged in the second column of table 9. A marked decrease in the acidity of the fresh fruit is apparent until the fruit reached about 22° Balling, after which no further decrease was observed. Also, the acid content of the grapes in 1936 was slightly higher than in 1935, a fact which accounts for the minor discrepancies in the continuity of the decrease in acid as shown in table 9.

The size of the fresh berries (table 9, third and fourth columns) was appreciably greater in 1935 than in 1936. An increase in size during the early part of the ripening period is, furthermore, indicated.

The drying ratios for both dehydrated and sun-dried lots decreased without a break in continuity from the greenest to the ripest lots. When the drying ratio of the Muscat is multiplied by the Balling degree, the product shows a definite trend to increase as the fruit becomes riper, in contrast to the results with Thompson Seedless (table 1), with which the product of Balling \times drying ratio shows no tendency to drift with the Balling. The difference in behavior of the two varieties in this respect is logically attributed to the presence of seeds in the Muscat and their absence in the Thompson Seedless. If the seeds in the Muscat are assumed to be nearly mature in the greenest fruit used and to change but little as the sugar content of the grapes increases, then the effect on the relation of the drying ratio to the Balling degree would be as observed in these tests.

The weight per 100 raisin berries is influenced both by the size of the fresh berries and by the drying ratio. Since the fresh berries were larger in 1935 than in 1936, and since the lots in the lower Balling classes are preponderantly from the 1935 experiments, whereas the higher Balling classes were mostly obtained in 1936, the size of raisin berries as the fruit becomes more mature progresses upward less regularly than if the tests could have covered the entire range of maturity in both years. Nevertheless, the figures of table 9 show a 50 per cent increase in size of the raisin berries from the greenest to the ripest fruit used. Since commercial grading with Muscat raisins is largely based on size, obviously the commercial quality improved gradually over the entire range of maturity studied.

TABLE 10
THE RELATION BETWEEN BAILING DEGREE OF THE FRESH GRAPES AND COMPOSITION OF THE RAISINS, IN MUSCAT OF ALEXANDRIA*

Degree Bailing of fruit	Sugars (per cent, as invert)		Acid (per cent, as tartaric)		Insoluble solids, (per cent)		Potassium (per cent K)		Phosphorus (per cent P)		Calcium (per cent Ca)		Magnesium (per cent Mg)	
	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried	Dehy- drated	Sun- dried
16.0	62.8	62.2	3.16	2.67	13.8	15.3	0.796	0.794	0.101	0.100	—†	—	—	—
17.1	64.7	63.8	2.93	2.21	11.8	13.6	0.773	0.784	0.098	0.099	0.074	0.076	0.080	0.083
18.6 and 18.7	64.8	64.2	2.60	2.02	12.8	13.1	—	—	—	—	—	—	—	—
19.1 and 19.2	66.5	65.9	2.18	1.82	11.5	12.0	0.700	0.771	0.094	0.098	0.062	0.073	0.024	0.026
19.7 and 20.6	67.2	65.5	1.83	1.66	11.3	11.7	0.701	0.774	0.089	0.097	—	—	—	—
21.3 and 21.4	68.0	66.9	1.65	1.50	10.6	11.7	0.652	0.670	0.090	0.095	0.059	0.070	0.019	0.026
22.4 and 22.7	69.4	68.0	1.60	1.44	9.5	11.2	—	—	—	—	—	—	—	—
23.1 and 23.3	68.2	67.4	1.53	1.34	10.9	10.5	0.665	0.706	0.082	0.087	0.072	0.072	0.017	0.020
24.7 and 25.4	68.8	67.2	1.43	1.28	10.1	10.1	0.668	0.713	0.086	0.087	0.067	0.061	—	0.019
27.0 and 27.5	68.7	68.0	1.24	1.18	10.0	10.6	0.665	0.694	0.086	0.088	0.077	0.073	0.024	0.024

* Data adjusted to the basis of 15 per cent moisture in the raisins.

† Dashes indicate data not available.

The weight per unit volume of the Muscat raisins (table 9) shows a clear increase in this measurement as the grapes became ripier, but an increase neither so regular nor so great as in Thompson Seedless (table 2).

In the early part of the ripening range the Muscat raisins showed a marked increase in sugar as the grapes became ripier. Grapes of 16.0° Balling produced raisins having 62.8 per cent and 62.2 per cent sugar respectively for the dehydrated and sun-dried lots, whereas raisins made from grapes of 23.1°–23.3° Balling had 68.2 and 67.4 per cent sugar (table 10). Beyond the 23° Balling stage of maturity the sugar content of the raisins did not increase further with more advanced maturity of the grapes.

The total titratable acid content of the raisins decreased with advancing maturity, rapidly at first, then more slowly, but continued over the entire range of maturity. Raisins made from grapes at 16.0° Balling had 3.16 and 2.67 per cent total acid as tartaric in the dehydrated and sun-dried lots respectively, those from grapes of 23.1°–23.3° Balling had 1.53 and 1.34 per cent acid, and those from grapes of 27.0°–27.5° Balling had 1.24 and 1.18 per cent. The acid content of the sun-dried lots was consistently lower than that of equivalent dehydrated lots.

The water-insoluble solids content of the Muscat raisins, which included much of the seed materials, decreased from 13.8 and 15.3 respectively in dehydrated and sun-dried lots made from grapes of 16.0° Balling to between 10 and 11 per cent from grapes of 23.1°–23.3° Balling; thereafter it decreased but little, if at all.

Potassium and phosphorus in the raisins (table 10) decreased slightly in percentage as the maturity of the fresh grapes advanced. The decrease is small but too consistent to be ignored. Calcium and magnesium in the raisins seem to remain about the same over the entire range of maturity of the fresh grapes.

When compared with Thompson Seedless (table 6) the Muscat raisins were slightly lower in potassium and phosphorus content, slightly higher in calcium, and about the same in magnesium.

SUMMARY

Experiments were conducted to determine how the maturity of the fresh grapes influences the drying ratio, the size of the raisin berries, the weight per unit volume, the titratable acidity, and the content of sugar, potassium, calcium, magnesium, and phosphorus in the raisins. Thompson Seedless (Sultanina) and Muscat of Alexandria grapes, picked at about weekly intervals, were dried by several methods, including most of the standard commercial procedures and certain others that are not

commercial. The stage of maturity is represented by degree Balling of the juice from the fresh grapes. The tests with Thompson Seedless covered a range of 18° to 29° Balling and with Muscat 16° to 27°.

As the maturity of the fresh Thompson Seedless grapes advanced, the drying ratio decreased regularly with the increase in Balling degree, so that the product of Balling degree \times drying ratio remained nearly constant. With the Muscat of Alexandria, the drying ratio decreased with advancing maturity of the grapes, but not proportionally, and the product of Balling degree \times drying ratio drifted upward with the Balling. The size of the raisin berries and the weight per unit volume of raisins in both varieties increased along with the maturity of the grapes.

During the early part of the range of maturity studied, the sugar content of the raisins increased, whereas the total titratable acidity and insoluble-solids content decreased. The rate of these changes lessened as maturity advanced. Changes in the sugar and insoluble-solids content of the raisins nearly or quite ceased after the midpoint in the range of maturity of the grapes was reached, although the acidity of the raisins continued to decrease slowly.

The potassium, calcium, and magnesium content of the Thompson Seedless raisins remained fairly constant, whereas the phosphorus content appears to have decreased somewhat with advancing maturity. In the Muscat raisins both the potassium and phosphorus decreased, with the calcium and magnesium content remaining about the same.

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THE EFFECT OF PRETREATMENT AND
SUBSEQUENT DRYING ON THE
ACTIVITY OF GRAPE OXIDASE

A. A. HUSSEIN, E. M. MRAK, AND W. V. CRUESS

THE EFFECT OF PRETREATMENT AND SUBSEQUENT DRYING ON THE ACTIVITY OF GRAPE OXIDASE¹

A. A. HUSSEIN,² E. M. MRAK,³ AND W. V. CRUESS⁴

THOMPSON SEEDLESS GRAPES usually darken during drying in the preparation of raisins. The intensity of this darkening depends to a considerable extent on the treatment of the fresh fruit prior to drying. Raisins prepared by drying grapes in the sunlight without other treatment are characteristically of a dark color similar to the clove-brown of Ridgway (1912).⁵ Raisins produced by the cold-dip, mixed-dip, soda-dip (hot lye), sulfur-bleach, or golden-bleach procedures, on the other hand, usually have a light color ranging in hue from cinnamon-buff to sepia as judged by the color standards of Ridgway. Hussein and Cruess (1940) investigated the properties of grape oxidase and suggested that oxidizing enzymes are involved to a considerable extent in the darkening of grapes during the preparation of raisins, and to some extent in the darkening of wines. These authors, however, limited their investigations to the enzyme preparation obtained from fresh, untreated grapes. There is no available published information concerning the effects of the various treatments used in the production of light-colored raisins on the oxidizing enzymes occurring in grapes.

A series of experiments was conducted during the 1939 season in order to determine the effects of the mixed-, soda-, and cold-dip pretreatments, and of sulfuring and drying, on the oxidase activity of raisins made from Thompson Seedless grapes.

EXPERIMENTAL PROCEDURE

Materials Used.—Thompson Seedless grapes were used in all experiments unless otherwise indicated.

The sulfur-bleach and cold-, mixed-, and soda-dip procedures employed were similar to those in commercial use as described by Mrak and Long (1941). The golden-bleach procedure was similar to that used in the preparation of sulfur-bleach raisins, except that the fruit was dried in a dehydrater having a relative humidity of 25 per cent at the hot end, and a dry-bulb temperature of 71.1° C (160° F).

The dipping preparations used were: soda dip, 0.5 per cent solution of

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⁵ See "Literature Cited" for complete data on citations which are referred to in the text by author and date of publication.

NaOH brought to 95° C (203° F); mixed dip, an emulsion containing 68 grams of K_2CO_3 , 34 grams of NaOH, 50 cc of California olive oil, and approximately 12 liters of tap water brought to 82.2° C (180° F); and cold dip, an emulsion containing 950 grams of an alkali mixture consisting of 95 grams of Na_2CO_3 , 855 grams of K_2CO_3 , 100 cc of California olive oil, and approximately 20 liters water at 20° C (68° F).

Freshly picked Thompson Seedless grapes were treated in one or another of the dipping preparations for various periods of time, then sulfured or dried according to the particular procedure used in commercial practice.

Enzyme Preparation.—Untreated, freshly dipped, sulfured, and dried grapes were tested for oxidase activity after first making an enzyme preparation from the various samples. The enzyme preparations and measurement were made according to the procedures of Hussein and Cruess (1940) as described briefly in the paragraph below. Treated grapes were stored at -17.7° C (0°F), and the raisins at 0° C (32° F) until used.

To make the enzyme preparation, samples were ground in a mortar containing white sand and acetone and were then filtered. This procedure was repeated a second and third time. The dilute acetone prevented browning, removed auto-oxidizable catechol compounds, tannins, some of the water-soluble materials, and precipitated the enzyme. The solid residue was then extracted with a 0.2 molar citrate buffer of pH 4.5, equal in volume in cubic centimeters to three times the weight in grams of the grape sample used. Then three volumes of 95 per cent alcohol were added and the mixture centrifuged. The resulting precipitate was suspended in the aforementioned citrate buffer.

Quantitative Measurement of Grape-Oxidase Action.—The colorimetric method of Bansi and Ucho (1926) as modified by Hussein and Cruess (1940), was used for the quantitative measurement of oxidase activity. This procedure is as follows: 1 cc of enzyme extract and 1 cc of 1 per cent guaiacol solution (by volume) in 50 per cent ethyl alcohol were added to a test tube containing 5 cc of 0.2 molar acetate buffer of pH 4.5. Then sufficient distilled water was added to make a total volume of 20 cc. Finally 1 cc of 0.1 N H_2O_2 was added to the same test tube after which the tube was held at 30° C (86° F) for 1 hour. The reaction was then stopped by the addition of 5 cc of glacial acetic acid. The peroxidase enzyme of the grapes catalyzes the oxidation of the guaiacol by the H_2O_2 , a reaction similar to that occurring during the browning of the grape flesh by oxidation catalyzed by the enzyme.

Hussein and Cruess (1940) estimated enzyme activity by observing the extent to which the extracts darkened. This was conveniently done

by measuring the light transmission with an Evelyn photoelectric colorimeter, with a filter having maximum transmission at 5,400 angstrom units. From the transmissions (T) were calculated values of $\log 1/T$, used as the measure of enzyme activity. The greater the value of $\log 1/T$ the greater is the enzyme activity.

EXPERIMENTAL OBSERVATIONS

Effect of Various Dips.—The effects of the type and time of dip used on enzyme activity of fresh grapes are shown in table 1. The enzyme

TABLE 1
EFFECT OF VARIOUS DIPPING TREATMENTS ON ENZYME ACTIVITY
OF THOMPSON SEEDLESS GRAPES

Type of dip	Dipping period	Per cent of light transmission	Log 1/T values for enzyme activity	Per cent increase or decrease in oxidase activity
Cold dip*	2 minutes.....	46.25	-0.335	- 2.6
	5 minutes†.....	59.00	-0.229	-34.8
	10 minutes.....	64.50	-0.190	-45.0
No dip (check).....	45.00	-0.347
Mixed dip‡	5 seconds†.....	40.00	-0.398	+15.8
	30 seconds.....	56.25	-0.248	-28.0
	60 seconds.....	75.75	-0.120	-64.5
No dip (check).....	45.50	-0.342
Soda dip (5 per cent solution of NaOH).....	5 seconds†.....	38.50	-0.415	+14.2
	30 seconds.....	95.25	-0.022	-94.0
	60 seconds.....	98.75	-0.004	-99.0
No dip (check).....	43.50	-0.362

* An emulsion containing 950 grams of alkali mixture (95 grams of Na_2CO_3 and 855 grams of K_2CO_3) and 100 cubic centimeters of olive oil and about 20 liters of tap water.

† Dipping periods commonly used in commercial practice.

‡ An emulsion containing 68 grams of K_2CO_3 , 34 grams of NaOH, 50 cubic centimeters of olive oil, and 12 liters of tap water.

activity of grapes treated in the cold dip decreased when the length of dipping period was increased. This decrease in enzyme activity, however, was not directly proportional to the length of dipping period used. The skin of grapes treated in the cold dip did not crack, even after 10 minutes' exposure, but much of the waxy bloom was removed. The amount removed varied according to the length of the dipping period. Each skin was covered with a thin layer of oil which caused the fruit to remain soft and pliable, even when dried. This oil coating may have acted as a layer retarding the entrance of oxygen into the flesh of the fruit, thereby preventing in some degree, darkening of the raisins by oxidation.

Immersion of grapes for an appreciable period of time in the hot dipping solutions reduced the enzyme activity, whereas dipping for a very short time increased enzyme activity. When the dipping period was increased to 30 seconds or more, enzyme activity decreased rapidly as shown in table 1. The most rapid decrease in enzyme activity occurred when the grapes were treated in the soda dip, while the slowest decrease in activity occurred when they were treated in the cold dip. The temperature of the dipping solution was undoubtedly an important factor in accounting for these differences. In order to determine the effect of heat alone on the enzyme activity, dipping tests were conducted in distilled

TABLE 2

EFFECT OF HOT-WATER DIPS ON ENZYME ACTIVITY IN THOMPSON SEEDLESS GRAPES

Temperature of dip, degrees Fahrenheit	Dipping period, seconds	Per cent of light transmission	Log 1/T values for enzyme activity	Per cent increase or decrease in oxidase activity
180.....	{ 5.....	45.1	-0.345	+18.0
	{ 30.....	69.0	-0.162	-43.0
	{ 60.....	88.2	-0.092	-70.5
No dip (check).....	52.0	-0.284
205.....	{ 5.....	48.2	-0.315	+17.5
	{ 30.....	95.2	-0.020	-92.5
	{ 60.....	98.2	-0.006	-98.5
No dip (check).....	54.0	-0.268

water at 82.2° C (180° F) and 96.1° C (203° F). The results were very similar to those obtained in the experiments with the soda and mixed dips. Grapes dipped for 5 seconds in hot water at 82.2° C (180° F) and 96.1° C (203° F) displayed an increase in enzyme activity similar to that observed in the mixed-dip and soda-dip experiments. When grapes were subjected to the hot-water treatments for 30 or 60 seconds, on the other hand, enzyme activity decreased greatly as indicated in table 2. The skins of most of the grapes subjected to the soda dip, the mixed dip or the 30- and 60-second hot-water dips cracked extensively. The most severe skin cracking occurred when the longest dipping periods were used; the skins of grapes subjected to the 5-second hot-water dip, did not crack. When a grape oxidase preparation was heated for various periods of time at 82.2° C (180° F) and 95° C (203° F) no activation effect was observed (table 3). The enzyme system was almost completely inactivated in 30 seconds. This indicates that the apparently increased activity, observed when grapes were treated in the soda and the mixed dips for short periods of time, was due to some other cause than oxidase

response alone. Further tests were conducted with Muscat grapes which are larger and have thicker skins than the Thompson Seedless variety. Although the Muscat grapes were dipped in water at 95° C (203° F) for various periods of time up to 60 seconds, in no case did the skins of these grapes show cracking. Furthermore, the data obtained (table 4) show that heating in water for very short periods of time did not increase

TABLE 3
EFFECT OF HEAT ON THE ENZYME PREPARATION OBTAINED FROM
THOMPSON SEEDLESS GRAPES

Heating period in seconds at 180° F	Per cent of light transmission	Log 1/T values for enzyme activity	Per cent decrease in oxidase activity
0 (check).....	88.00	-0.056	...
2.....	88.50	-0.054	3.5
5.....	89.25	-0.050	8.9
10.....	88.50	-0.054	3.5
15.....	89.50	-0.046	17.6
20.....	95.00	-0.022	60.7
30.....	98.75	-0.005	91.1

TABLE 4
THE EFFECT OF HOT-WATER DIPS ON ENZYME ACTIVITY
IN MUSCAT GRAPES

Dipping period in seconds at 203° F	Per cent of light transmission	Log 1/T values for enzyme activity	Per cent decrease in oxidase activity
0 (check).....	39.0	-0.409	..
5.....	47.2	-0.323	22.0
10.....	86.0	-0.065	84.0
20.....	91.2	-0.039	90.7
60.....	95.2	-0.022	94.2

enzyme activity. The enzyme system was almost completely inactivated after 60 seconds of heating. This indicates that skin differences between the two varieties may be partially responsible for the variations in oxidase responses to the dipping treatments of short duration. Variations in oxidase distribution within the individual berry, as well as varietal differences in size of the berries, may also be factors accounting for the observed differences in effects of the heated dips on the oxidase activity of the two varieties.

In order to compare the distribution of enzyme activity in Thompson Seedless and Muscat grapes, individual berries were peeled and the Muscats were seeded. Table 5 shows that enzyme activity was greater

in the skins than in the flesh of the two varieties of grapes used. A much greater difference between enzyme activity in skin and flesh was observed in the Thompson Seedless than in the Muscat grapes. Enzyme activity in Muscat grapes was slightly greater in the skin than in the flesh. In Thompson Seedless, on the other hand, enzyme activity in the skins was over 31 times as great as that in the flesh. The skins of Thompson Seedless grapes showed more activity than either the skin or the flesh of Muscat grapes. The flesh of the former, however, showed less activity than either the skin or flesh of the latter. The relative richness in oxidase of skin as observed here agrees with the data of Hussein and Cruess

TABLE 5
COMPARISON OF ENZYME ACTIVITY OF SKIN AND FLESH OF THOMPSON
SEEDLESS AND MUSCAT GRAPES

Variety of grape	Portion of grape tested	Per cent of light transmission	Log 1/T values for enzyme activity	Weight ratio of skin to flesh	Oxidase activity ratio of skin to flesh*
Thompson Seedless..	{ Skin.....	61.00	-0.215	0.113:1	31.1:1
	{ Flesh.....	82.50	-0.083		
Muscat.....	{ Skin.....	76.25	-0.118	0.101:1	7.75:1
	{ Flesh.....	75.00	-0.122		

* Solutions used in measurement of enzyme activity of Thompson Seedless skins were diluted twelve times and that for Muscat skins eight times. Corrected values for activity ratio of skin to flesh are given in the last column. The activity ratio of Muscat flesh to Thompson Seedless flesh (corrected value) = 1.47:1; and of Muscat skin to Thompson Seedless skin (corrected value) = 0.37:1.

(1940) concerning the location of the enzyme in the grape. This observed unequal enzyme distribution is probably concerned, to some extent at least, with the variations in enzyme responses when Thompson Seedless and Muscat grapes were treated in the hot-water dips. It may also account for the fact that Muscat grapes that retain a light color have not been produced successfully on a commercial scale by use of the cold, mixed, or soda dips without a subsequent sulfuring treatment.

Effect of Sulfuring.—Sulfur-bleached raisins were dried to a moisture content of about 15 per cent. The oxidase activity in finished raisins varied greatly with the period of exposure and concentration of SO₂ used in the sulfuring treatment. The data in table 6 show that the enzyme activity in the sulfur-bleached raisins decreased with increase in length of the sulfuring period. In these experiments, as in commercial practice, the lightest-colored raisins were obtained when grapes were sulfured for 2 hours and the darkest when they were sulfured for 1 hour or less. Table 7 indicates that the concentration of SO₂ in the sulfuring house at the time of sulfuring also affects the enzyme activity of raisins treated by this method.

Raisins prepared by drying grapes sulfured at the higher concentrations of SO_2 , for a given period of time had less enzyme activity than those sulfured at lower concentrations for the same period of time. Apparently the time of exposure and concentration of SO_2 during sulfuring are both important in diminishing oxidase activity in sulfured raisins. Hussein and Cruess (1940) found that very high concentrations of SO_2

TABLE 6
EFFECT OF TIME OF SULFURING ON THE OXIDASE ACTIVITY
OF SULFUR-BLEACHED RAISINS

Sulfuring period, minutes*	SO_2 in raisins, p.p.m.	Log 1/T values for enzyme activity†	Per cent decrease in oxidase activity	Color grade of the finished raisins‡
0 (check)	-0.025	...	Poor
30	150	-0.023	7.0	Poor
60	300	-0.016	35.7	Poor
90	400	-0.010	59.5	Fair
120	570	-0.005	79.4	Good

* The concentration of SO_2 in the sulfuring compartment was 1.5 per cent by volume, and the temperature, $105^\circ\text{--}120^\circ\text{F}$.

† Represents activity calculated to 1 gram of dry weight.

‡ Color grade judged from standpoint of salability as sulfur-bleached raisins.

TABLE 7
EFFECT OF CONCENTRATION OF SO_2 DURING SULFURING ON THE OXIDASE
ACTIVITY OF SULFUR-BLEACHED RAISINS

Concentration of SO_2 in per cent by volume in sulfuring compartment*	SO_2 in raisins, p.p.m.	Log 1/T values for enzyme activity†	Per cent decrease in oxidase activity	Color grade of the finished raisins‡
Check	-0.025	...	Poor
0.75	270	-0.020	18.7	Poor
1.50	570	-0.006	77.9	Good

* The length of the sulfuring period was 120 minutes and the temperature $105^\circ\text{--}120^\circ\text{F}$.

† Represents activity calculated to 1 gram of dry weight.

‡ Color grade judged from standpoint of salability as sulfur-bleached raisins.

were required to inactivate a grape-enzyme preparation. Oxidase activity decreased gradually as the concentration of SO_2 added to the solution was increased from 0 to 5,580 p.p.m., but was not entirely inhibited at any concentration used. It is difficult to understand why the enzyme preparation should be so resistant to SO_2 . Possibly other factors such as physical condition of the grapes, maturity, and temperature complicate the results.

Effect of Drying.—The treatment of grapes preliminary to drying is the same for golden-bleached and sulfur-bleached raisins. Both are lye-dipped and sulfured; but the former are then dehydrated and the

latter are exposed to the sun for a short time and later dried in the shade. The two products, however, are different in appearance and storage qualities. Sulfur-bleached raisins usually darken more rapidly in storage than do the golden-bleached; this may be attributed to some extent to the higher moisture content in the former. Nevertheless it was thought that oxidase may play a part in this darkening. Consequently, grapes from each of two lots were dehydrated and shade-dried and then compared for oxidase activity. Table 8 shows that the enzyme activity in the

TABLE 8
EFFECT OF SUN-DRYING AND DEHYDRATION ON OXIDASE ACTIVITY
IN THE DRIED PRODUCTS

Drying procedure	Per cent of light transmission	Log 1/T values for enzyme activity	Ratio of activity of dehydrated to sun-dried
Dehydrated at 160° F.....	90.75	-0.042	0.188:1
In sun 1 day and then dried in the shade.....	59.75	-0.224	
Dehydrated at 160° F.....	88.75	-0.052	0.213:1
In sun 1 day and then dried in the shade.....	57.00	-0.244	

dehydrated product was approximately one fifth of that of shade-dried. This variation in oxidase activity may account for some of the differences in the storage qualities of the two types of raisins.

SUMMARY

Oxidase enzymes cause discoloration of grapes and raisins under certain conditions. Experiments have been conducted to determine the effect of various dipping, sulfuring, and drying procedures on this activity. The commercial cold-, mixed-, and soda-dip treatments decreased the oxidase activity when immersion periods of sufficient length were used. Oxidase activity was stimulated by very short, soda, mixed, and hot-water dips. Sulfuring decreased the oxidase activity, approximately in proportion to the period of exposure and concentration of SO₂ used during sulfuring. Raisins prepared by dehydration had about one fifth the oxidase activity of sulfured grapes dried in the shade, probably because of the relatively high temperature used for dehydration.

The diminishing effect on oxidase activity of some of the commercial dipping treatments may account for the production of light-colored raisins without the use of SO₂.

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SOME FACTORS AFFECTING THE BURNING
OF SULFURS USED IN SULFURING
FRUITS

C. S. BISSON, H. W. ALLINGER, AND H. A. YOUNG

SOME FACTORS AFFECTING THE BURNING OF SULFURS USED IN SULFURING FRUITS¹

C. S. BISSON,² H. W. ALLINGER,³ AND H. A. YOUNG⁴

DURING THE 1936 season, growers in various districts in California were experiencing some difficulty in sulfuring the fruit to be dried. Long, Mrak, and Fisher⁵ found that the difficulties of that season were merely a recurrence of a series of yearly troubles. These investigators determined that some of the samples of sulfur in question burned 90 to 100



Fig. 1.—Illustrations of slag resulting from incomplete burning: *A*, light-colored slag from a high-grade sulfur indicating that the fire was smothered through insufficient ventilation; *B*, dark-colored slag from a low-grade sulfur indicating that the fire was smothered by carbon or carbonaceous matter which floated to the surface of the molten sulfur.

per cent, whereas many others burned anywhere from 10 to 50 per cent. With the poor-burning sulfurs the result was reduced quality of the product, delay in operations during the drying season, and an actual loss of sulfur through failure to burn.

Poor-burning sulfurs develop, over the burning, molten surface, a black film that decreases the rate of vaporization of the sulfur by shielding the molten sulfur from direct contact with the flame, which grad-

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⁵ Long, J. D., E. M. Mrak, and C. D. Fisher. Investigations in the sulfuring of fruits for drying. California Agr. Exp. Sta. Bul. 636:1-56. 1940.

ually decreases the burning area and finally extinguishes the flame. The unburned sulfur solidifies on cooling and forms a dark hard cake or slag (fig. 1), not easily removed from the pans.

Though a black variety of sulfur can be produced,⁶ the sulfur samples tested in the experiments reported here were not subjected to the same conditions as those given for producing the black variety.

EXPERIMENTAL RESULTS

Identification of Contaminants Affecting Burning.—Chemical tests on the composition of this black film on cakes from commercial sulfuring houses showed, after the included sulfur had been driven off by controlled heat treatment, that the film consisted largely of carbon or carbonaceous material, with some siliceous matter and iron oxide, the second probably coming from dust, and the latter chiefly from the iron pans in which the sulfur was burned by the growers.

When this work was first undertaken it was planned to be carried out entirely in the laboratory. The results obtained were such, however, that it was decided to follow up the laboratory experiments with field tests conducted in a commercial sulfuring house. All of the sulfurs used in the following experiments were of commercial grade and of unknown purity.

Laboratory Experiments.—Tests were directed toward investigating the role that the impurities found in the black film or scum play in reducing the burning of sulfurs. The method consisted in adding varying small amounts of iron oxide, siliceous compounds, and carbonaceous matter to samples of sulfur no. 1 that normally burned 99.7 per cent, and observing how these added materials affected the reduction of the amount of sulfur burned.

In working out the procedure to be followed in these tests, it was found that the methods adopted would be empirical. That is, the results would depend considerably on factors influencing the temperature of the sulfur and the film formation—for example, the size of the sample used; the control of air drafts; the size, shape, and composition of the container; and the nature of the surface on which the container was placed (transite, wood, sand, and the like).

In a series of tests, 10-gram samples of sulfur gave the most consistent results. These tests also showed that 2.5-inch porcelain evaporating dishes are more satisfactory than 2-inch straight-sided aluminum dishes for the burning of sulfur. Transite board proved to be the most satis-

⁶ Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. 10, p. 34. Longmans, Green and Company, New York, N. Y. 1930.

factory support for the sulfur dishes. Careful shielding of the containers was necessary to insure consistently good burning.

All samples were burned from a cold start (except where noted) under optimum conditions. That is, the cold sulfur was carefully lighted with

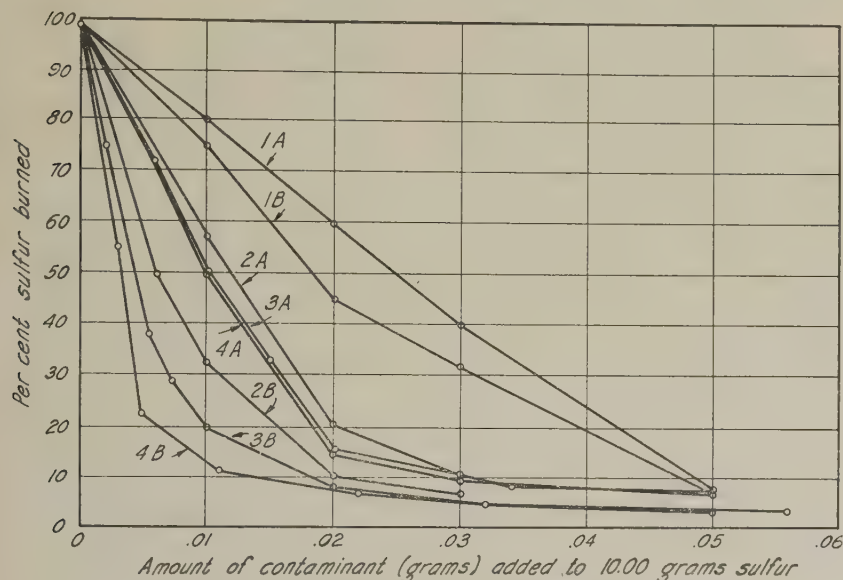


Fig. 2.—Effect of lubricating oil (medium) and of fuel oil on the percentage of sulfur burned:

Curve 1A, fuel oil added; burned at once without mixing.

Curve 2A, fuel oil added; burned after one thorough mixing.

Curve 3A, fuel oil added; burned after 4 hours and three thorough mixings during the interval.

Curve 4A, fuel oil added; burned after 24 hours and four thorough mixings during the interval.

Curve 1B, lubricating oil added; burned at once without mixing.

Curve 2B, lubricating oil added; burned after one thorough mixing.

Curve 3B, lubricating oil added; burned after 4 hours and three thorough mixings during the interval.

Curve 4B, lubricating oil added; burned after 24 hours and four thorough mixings during the interval.

a match, the match discarded, and the dish then placed on a transite board and shielded from drafts.

Effect of Various Admixtures on Burning.—In the first experiments on the effect of impurities on sulfur burning, small amounts of ignited dust or iron oxide, varying from 0.005 to 0.05 gram, were mixed with 10-gram samples of sulfur no. 1, and the mixtures burned. These contaminants in the quantities used did not significantly affect the burning of the sulfur. Judging from these results, tests would have to be confined

to a study of the difficulty originating from the presence of carbonaceous matter in commercial sulfurs.

In order to determine how molten sulfur affects the volatile vapors of carbon compounds, hot vapors from boiling fuel oils were bubbled through hot molten sulfur in a test tube. The sulfur darkened quickly;

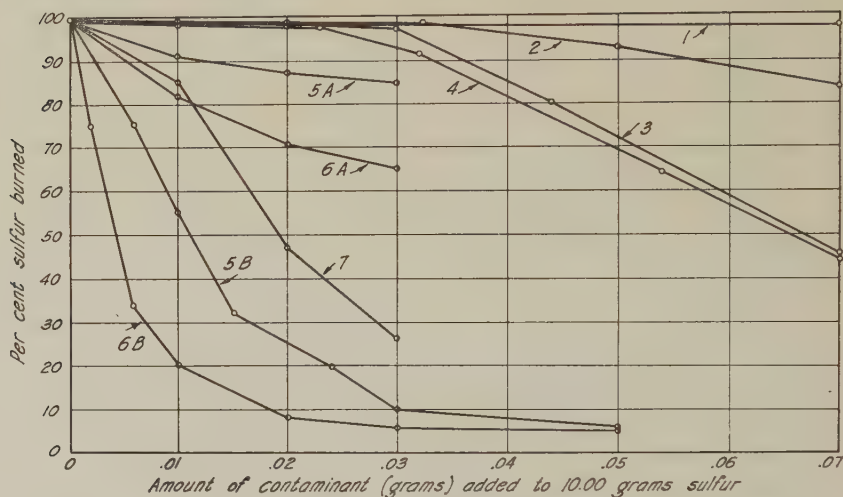


Fig. 3.—Effect of sack lining, burlap sacking, newspaper, sawdust, linseed oil, and rosin on the percentage of sulfur burned:

Curve 1, sack lining added (finely cut); burned after 1 hour with one thorough mixing.

Curve 2, burlap sacking added (finely cut); burned after 1 hour with one thorough mixing.

Curve 3, newspaper added (finely cut); burned after 1 hour with one thorough mixing.

Curve 4, sawdust added; burned after 1 hour with one thorough mixing.

Curve 5A, linseed oil added; burned at once without mixing.

Curve 5B, linseed oil added; burned after 4 hours with three thorough mixings during the interval.

Curve 6A, rosin dust added; burned at once without mixing.

Curve 6B, rosin dust added; burned after 4 hours with three thorough mixings during the interval.

Curve 7, paraffin added (finely cut); mixed in, and burned after 3 hours.

and a black film was formed over the sulfur and on the sides of the test tube above the sulfur, clearly indicating the breakdown of the fuel-oil vapors in their passage through the hot sulfur. With these results as a basis, various types of materials (lubricating oil, fuel oil, kerosene, gasoline, linseed oil, turpentine, rosin, organic acids, sawdust, paper scraps, sacking, and the like) were added to 10-gram samples of sulfur no. 1, and the resulting mixtures were burned. Some of these mixtures were burned immediately without mixing, whereas others were mixed and allowed to stand as described in figures 2 to 4.

Figure 2 shows the effect of adding varying amounts of lubricating oil (medium) and fuel oil to sulfur no. 1. As the curves show, the more thoroughly the added materials are mixed with the sulfur and the longer the time allowed for diffusion of the added substances, the lower is the percentage of sulfur burned; the greatest decrease occurred in mixtures

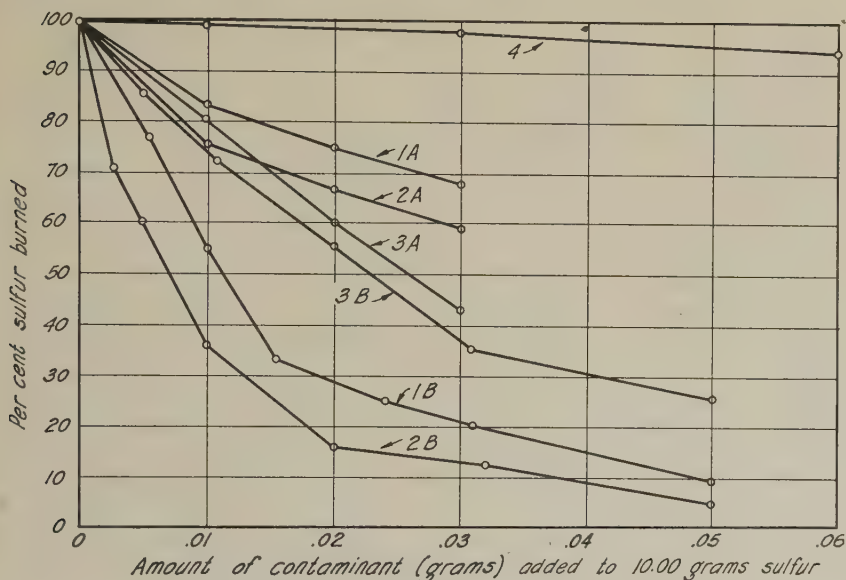


Fig. 4.—Effect of gasoline, turpentine, oleic acid, and stearic acid on the percentage of sulfur burned:

Curve 1A, stearic acid added; burned at once without mixing.

Curve 1B, stearic acid added; burned after 4 hours and after three thorough mixings during the interval.

Curve 2A, oleic acid added; burned at once without mixing.

Curve 2B, oleic acid added; burned after 4 hours and after three thorough mixings during the interval.

Curve 3A, turpentine added; burned at once without mixing.

Curve 3B, turpentine added; burned after 4 hours and three thorough mixings during the interval.

Curve 4, gasoline added; burned after 2 hours and two thorough mixings during the interval.

where the weight of the added impurity was less than 0.01 gram. The slope of the curve gradually decreased when amounts up to 0.05 gram were added. In appearance and in effect on burning, the film or scum formed by these materials resembles that observed when low-grade commercial sulfurs were burned.

Figure 3 manifests a marked difference in the effect of certain added materials on the reduction of the percentage of sulfur burned. The curves for linseed oil and rosin show much the same slope as the oils in figure 2.

They show the same large initial drop in percentage of sulfur burned when very small amounts are added and well mixed in, and a much smaller drop when larger amounts up to 0.05 gram are added.

The picture is very different for the other materials in figure 3—when sack lining, newspaper scraps, burlap sacking, and sawdust are added. Sack lining, used by some sulfur companies to line burlap sacks for the better protection of their product, had very little effect on the burning

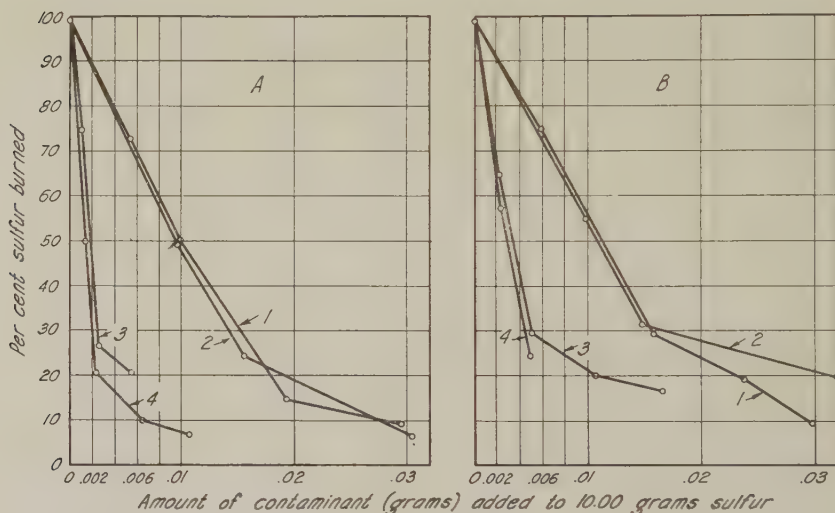


Fig. 5.—A, Effect of fuel oil on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.

Curve 2, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.

Curves 3, 4, field test, in 1940; four thorough mixings, and let stand overnight.

B, Effect of linseed oil on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.

Curve 2, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.

Curves 3, 4, field test, in 1940; four thorough mixings, and let stand overnight.

of sulfur when added in finely divided amounts up to 0.07 gram. Newspaper scraps, sawdust, and burlap lowered the percentage of sulfur burned very little when present in amounts less than 0.03 gram; but in larger amounts, up to 0.07 gram, they reduced the amount of sulfur burned to about one half. Since sugar had practically no effect on the burning of sulfur, its curve is not given in the figure.

Figure 4 shows the effect of stearic acid, oleic acid, turpentine, and gasoline in unmixed and thoroughly mixed samples. The unsaturated acid, oleic, shows the largest reduction in the amount of sulfur burned. The test with gasoline affected the burning of sulfur very little, probably because of its high volatility.

Field Experiments.—The laboratory experiments furnished striking data on the deleterious effect of small amounts of certain carbon and carbonaceous material on the burning qualities of sulfur. The next step in this work was to learn how data obtained under laboratory conditions checked with those secured under field conditions, where large quantities of sulfur (4 or more pounds) are burned in commercial sulfuring houses. Accordingly a three-compartment sulfuring house⁷ on the Davis campus

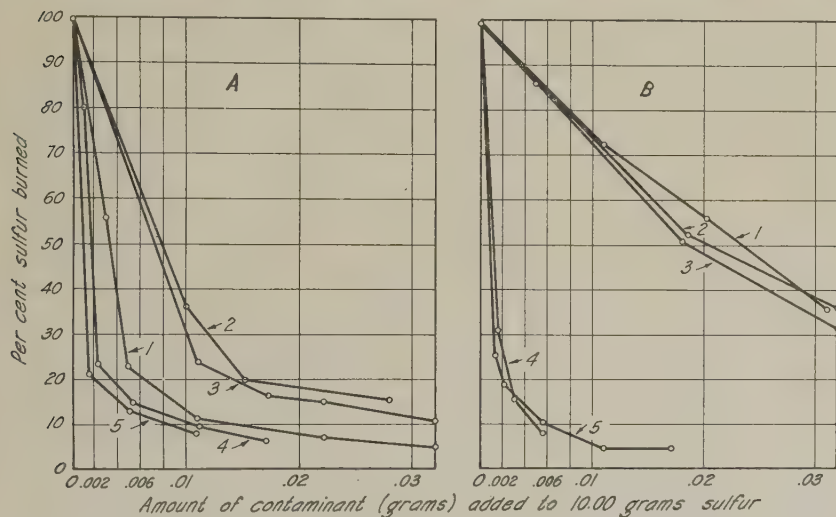


Fig. 6.—A, Effect of lubricating oil on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.

Curves 2, 3, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.

Curves 4, 5, field test, in 1940; four thorough mixings, and let stand overnight.

B, Effect of turpentine on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.

Curves 2, 3, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.

Curves 4, 5, field test, in 1940; four thorough mixings, and let stand overnight.

was used for these tests. A high-grade sulfur (no. 6), which burned 99.75 per cent, was used as a base to which were added varying amounts of lubricating oil, fuel oil, linseed oil, turpentine, newspaper, sawdust, and burlap sacking. Since in the 1938 laboratory work sulfur no. 1 was used, some laboratory tests on sulfur no. 6 were made for comparison. The amount of sulfur used in each of the field trials was 1,800 grams (nearly 4 pounds). These samples were burned in clean metal pans in an empty sulfuring compartment.

To facilitate comparison between the laboratory and field results, the

⁷ This sulfuring house was constructed according to the design by Long, Catlin, and Nichols, given in California Agricultural Extension Service Farm Building Plan C-173. 1934.

latter data were recalculated to fit the scale used in the graphs of the 1938 laboratory experiments. Figures 5 to 7 show the data in this form.

The effect of contaminants on burning were on the whole greater in the field than in the laboratory. As figure 5, *A*, shows, approximately a

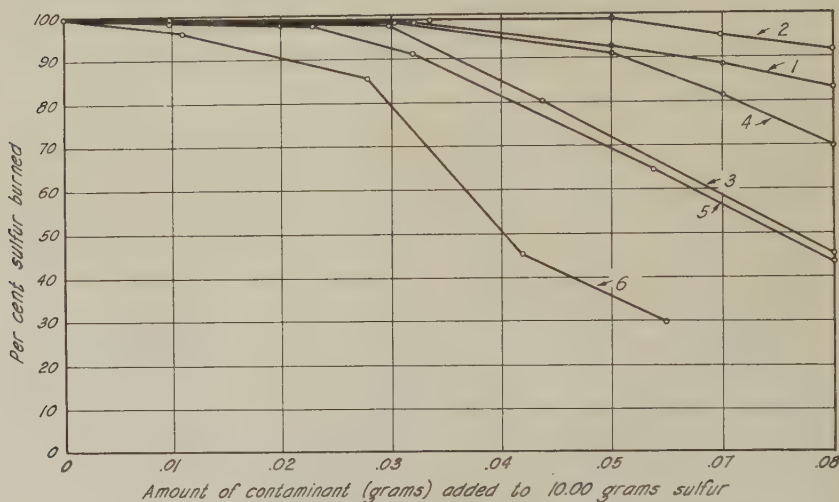


Fig. 7.—Effect of burlap sacking, newspaper, and sawdust on the percentage of sulfur burned:

- Curve 1, burlap sacking added. Laboratory test, in 1938, with sulfur no. 1.
- Curve 2, burlap sacking added. Field test, in 1940, with sulfur no. 6.
- Curve 3, newspaper cuttings added. Laboratory test, in 1938, with sulfur no. 1.
- Curve 4, newspaper cuttings added. Field test, in 1940, with sulfur no. 6.
- Curve 5, sawdust added. Laboratory test, in 1938, with sulfur no. 1.
- Curve 6, sawdust added. Field test, in 1940, with sulfur no. 6.

50 per cent reduction in the burning of sulfur was caused by 0.01 gram fuel oil in the laboratory tests, whereas in the field only 0.0014 gram (one seventh as much) was needed to produce the same reduction. In figure 5, *B*, 0.016 gram linseed oil lowered burning to about 30 per cent in the laboratory, while in the field 0.0052 gram reduced the burning to 24–29 per cent in two series of trials. Still more striking were the tests with turpentine in figure 6, *B*. With 0.02 gram turpentine in the laboratory, sulfur burned approximately 55 per cent; but in the field only 0.001 gram (one twentieth as much) was needed to bring about a similar reduction. Lubricating oil in figure 6, *A*, does not show so great a difference between the 1938 laboratory tests and the 1940 field results. With 0.0048 gram lubricating oil, sulfur burned 22.5 per cent in the laboratory; and in the field 0.0014 gram produced the same result. The curves obtained in the 1938 and the 1940 laboratory tests for lubricating oil do not check as they do for fuel oil, linseed oil, and turpentine. This dif-

ference may be caused by a somewhat different grade of lubricating oil used in 1940. If the 1940 data are used for comparison, the difference between laboratory and field results is greatly increased.

In figure 7, sawdust in the field experiments reduced the burning of sulfur much more than it did in the laboratory. This is not the case with newspaper cuttings and burlap sacking, whose field curves lie above those of the laboratory. No satisfactory explanation was found for this reversal.

In the field the sulfur is burned in an enclosed chamber where the air intake is greatly reduced and the sulfur dioxide gas accumulates to a large extent, whereas in the laboratory the sulfur is burned in the open with free access to air and with no accumulation of gases. This difference in burning conditions perhaps explains the greater reduction of contaminated sulfur burned in the field experiments.

Sources of Contamination.—As for the sources of contamination of sulfurs in actual practice, the contaminants may be matches, rags, or papers dropped carelessly into the sulfur after igniting it; from admixture with impure slag in the burners from pervious burnings; from oily floors on which the sacks of sulfur may have been stored; or from burlap sacks containing some oily matter. In the two last-mentioned instances such contaminating materials will penetrate the sulfur in the sacks by diffusion and reduce the percentage of sulfur that will burn freely.

Experiments (made in 1938) in which samples of sulfur no. 1 were placed in the vapors arising from the surface of heavy diesel fuel oil held at room temperature (25° C or 77° F) showed, in every case, a noticeable increase in black film formation and a decrease in the percentage of sulfur burned when compared with that of the original sulfur sample. One sample stored for 6 days over the fuel oil showed a decrease of 9 per cent in the percentage of sulfur burned. These results indicate that the oil vapor is absorbed by the sulfur at ordinary temperatures.

Another source of contamination may go back to the origin and preparation of the sulfur. In the preparation, traces of hydrocarbon oils may be introduced from pipes used to convey steam and from contamination by traces of oil from contiguous strata. Several fractional distillations^{*} are required to remove the last traces of hydrocarbons from sulfur during preparation or refining.

This investigation did not aim to determine whether the carbonaceous matter in poor-burning commercial sulfurs is caused by insufficient refining, subsequent contamination, or both.

Purification of Contaminated Sulfur.—A method for freeing sulfur from interfering contaminants consists in heating the crude sulfur under

^{*} See page 19 of citation given in footnote 6.

pressure over a temperature range of 255° to 320° C for a sufficient period to complete the chemical reactions. The excess sulfur is then sublimed from the residue.

Tests were made with solvents to ascertain whether contaminating materials could be removed by extraction. As table 1 shows, the solvent action of ethyl ether was somewhat better than that of petroleum ether on the impurities in the sulfur. Commercial sulfur no. 4 normally burned 39.0 per cent; but when extracted with petroleum ether it burned 83.7 per cent, and with ethyl ether, 89.5 per cent. The next greatest effect was with no. 5, which burned 61.0, 82.4, and 91.2 per cent, respectively.

TABLE 1
PERCENTAGE OF SULFUR BURNED BEFORE AND AFTER THREE-HOUR
EXTRACTION OF TEN-GRAM SAMPLES WITH SOLVENTS

Sulfur no.	Before extraction	After extraction	
		With petroleum ether	With ethyl ether
2.....	74.0	84.5	90.5
3.....	70.0	91.0	92.2
4.....	39.0	83.7	89.5
5.....	61.0	82.4	91.5

Extractions with methylene chloride and ethylene chloride were not successful; 20 to 25 per cent of the sulfur dissolved, and difficulty was also experienced in removing the last traces of the solvents from the undissolved sulfur.

Extraction of poor-burning sulfurs with petroleum and ethyl ethers increased the percentage of sulfur burned up to 90 per cent or above; but the volatility and inflammability of these solvents and the difficulty of their complete removal from the treated sulfur makes this treatment non-feasible for growers as a means of purifying sulfur.

Effect of High Temperature on Poor-burning Sulfurs.—Another method of increasing the burning quality of low-grade sulfurs has more promise. As stated before, scum formation decreases the burning area, lowers the temperature of the molten sulfur, and causes the flame to die out. To study the effect of maintaining the temperatures of the dishes containing the burning sulfur at higher levels, samples of medium-burning and poor-burning commercial sulfurs were placed in a sandbath; and the bath was heated to 300° C (572° F) and maintained at that temperature after igniting the sulfurs. The results are given in table 2. In all cases the percentage burned was increased. Judging from these tests, if the temperature of the pans containing poor-burning sulfurs can be

maintained at about 200° C, these sulfurs will burn almost completely. Even at 150° C sulfurs nos. 2 and 3 burned 98.1 and 99.6 per cent (table 2). Preventing or minimizing the loss of heat from the pans is definitely indicated. Some growers have placed asbestos or other insulating material around the sulfur pans, and thereby obtained some measure of success in increasing the amount of sulfur burned. Application of heat

TABLE 2
EFFECT OF RAISING TEMPERATURE OF SULFUR ON PERCENTAGE BURNED

Sulfur no.	Room temperature 25°-30° C	Sandbath maintained at		
		300° C	200° C	150° C
2.....	74.0	99.9	99.6	99.6
3.....	70.0	99.9	99.7	98.1
7.....	34.8	99.9	99.6	96.2
8.....	34.0	99.9	99.7	96.5

to the sulfur containers by a regenerative heating process holds some promise of usefulness, but this process requires careful control of the amount of air used to burn the sulfur completely.

SUMMARY

As chemical tests showed, the black film consisted almost entirely of carbon or carbonaceous material, with small amounts of siliceous matter and iron compounds.

Small amounts of inorganic materials such as dust and iron oxide have practically no effect on reducing the percentage of sulfur burned.

Judging from experiments on black-film formation, carbon or carbonaceous matter originated most likely from the interaction of molten sulfur or hot sulfur vapors, with traces of certain organic impurities. Of the widely varying materials tested, the petroleum oils and turpentine produced the most pronounced effect on film production and also showed the greatest reduction of sulfur burned, whereas cellulose materials had the least effect.

Under field conditions the percentage of burning of contaminated sulfur was considerably less than in the laboratory. This decrease in combustibility was probably due to the limited access of air and the accumulation of sulfur dioxide in the sulfur chamber.

Extracting or washing poor-burning sulfurs with suitable solvents was found to increase the percentage of sulfur burned, but this method is not economical in farm practice.

Samples of sulfur stored 2 to 6 days in an atmosphere of vapors arising from fuel oil were found to absorb sufficient amounts of volatile carbon compounds to increase the black-film formation and decrease the amount of sulfur burned. This fact may be important in defining proper conditions for the storage of sulfur.

Raising the temperature of the sulfur container will almost completely burn a contaminated sulfur.